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PENTAMMINOCOBALT(III) COMPLEXES IN ANHYDROUS HYDROGEN FLUORIDE

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SUMMARY

Reactions of the cobaltammine cations $[Coa_5X]^{3+}$ (a = NH_3; X = OH_2, Cl^-, Br^-, ONO_2^-, OCO_2^{2-}, ONO^-, NO_2^-, CN^- and N_3^-) with anhydrous HF have been investigated by n.m.r. and visible spectroscopy. The solvent attacks and displaces all of the ligands except NH_3, Cl^-, Br^- and CN^- with the formation of $[Coa_5F]^{2+}$ ion. In the presence of free HCl fluoride is displaced from the coordination sphere to form $[Coa_5Cl]^{2+}$. Solvolysis of coordinated nitrato, carbonato, nitrito and nitro by HF proceeds via aquopentamminocobalt(III) as intermediate. Ligand displacement reactions when X = OH_2, NO_2^- and N_3^- are halted at -60°C; however, the azido ligand undergoes protonation and $[Coa_5(N_3H)]^{3+}$ is formed.

INTRODUCTION

Most transition metal complex compounds undergo protonation in anhydrous hydrogen fluoride (AHF): this type of reaction is commonly followed by a solvolysis in which metal-ligand bonds are cleaved and the metal fluoride is generated. In only a few instances is it known that a new metal-ligand bond is formed in this medium although metal- and ligand-protonation are also alternatives [1].

The behaviour of cobalt(III) ammine complexes in sulphuric and chlorosulphuric acids has been investigated by Jolly and co-workers, who have found that the pentamminocobalt(II) entity is inert to solvolysis. They have reported that the fate of a number of $[Coa_5X]^{3+}$ ($X \neq$ a = NH_3) complexes in sulphuric is a function of the nature of the ligand X and of the water-content of the sulphuric acid: the only stable product of reaction in 100%

sulphuric acid is the bisulphato complex [2]. In a subsequent paper [3] it was implied that complexes with X=CN^- and NCS^- show some stability in this medium.

This paper describes the use of AHF as a solvent for such complexes and for their solvolysis products: the reactions are conveniently followed by ^1H n.m.r. and, to a lesser extent, visible spectroscopy. The ammine p.m.r. linewidths in HF, although unusually broad at room temperature, are narrower at temperatures between -40° and $-70^\circ C$, under which conditions several solvolytic reactions can be arrested. The solubilities of most ammine complexes are highly favourable even at the freezing point of the solvent ($-83.58^\circ C$), and the stability of the pentamminocobalt(III) entity in solution at room temperature is such that neither tetrammine nor paramagnetic complexes were detectable after several months.

EXPERIMENTAL

Materials and Techniques

The following cobalt(III) ammine complexes were prepared by standard methods [4,5] and analysed for C, H and N: $[Coa_6]Cl_3$; $[Coa_5X]Cl_2$, X=Cl^-, N_3^-, ONO^-, NO_2^-, CN^-; $[Coa_5Br]Br_2$; $[Coa_5CO_3]NO_3.H_2O$; $[Coa_5Y](NO_3)_2$, Y= N_3^-, NO_3^-; $[Coa_5H_2O](NO_3)_3$. Hydrogen fluoride (I.S.C. Chemicals).) was manipulated on a copper-PCTFE vacuum line.

Solutions for ^1H and ^{19}F n.m.r. spectroscopy were prepared in PCTFE spaghetti tubing; between 0.3 and 0.5ml. of HF was condensed on to each sample of complex (100mg) and the frozen mixture was isolated by heat-sealing the plastic tube. All the above complexes dissolved in HF at $-60^\circ C$ and ^1H spectra were measured at this temperature, unless it is otherwise stated. Each pentammino complex showed two resonances with chemical shifts δ_4 and δ_1, having intensities in the ratio 4:1. Ammonium hydrogen difluoride (ca 1mg) was the internal proton standard, 5.82 ppm, in all these solutions; it has been assumed that Me_4N^+ in liquid HF resonances 3.13ppm downfield from TMS [6]. Fluorine n.m.r. spectra were calibrated by sample substitution.

Absorption spectra in the visible region were measured on solutions containing approximately 9mg complex in 1ml AHF in a PCTFE tube (6.5 mm i.d): this tube was inserted in a conventional 10mm glass cell and the space around the tube was filled with water. The range scanned was 400-700nm.

Apparatus

N.m.r. and visible spectra were recorded on a Varian HA100 and a Perkin-Elmer 402 spectrometer, respectively.

Preparation of [Coa$_5$F](PF$_6$)$_2$

Carbonatopentamminocobalt(III) nitrate hydrate (1g) was treated with excess AHF in a PCTFE reactor and the solution allowed to stand for 24 hr. Excess solvent and the other volatiles were removed in vacuo to leave a sticky residue; this residue was treated with a saturated solution of NH_4PF_6 in 40% hydrofluoric acid, whereupon a pink solid separated out. This product was washed with hydrofluoric acid and dried in vacuo over KOH. Yield 1.4g. Analysis: Found: H, 3.61; N, 15.08%. $CoH_{15}N_5F_{13}P_2$ requires H, 3.31; N, 15.46%.

Solvolysis of [Coa$_5$Cl Cl$_2$] in AHF

Chloropentamminocoablt(III) chloride (0.99g) was treated with excess AHF in a PCTFE reactor. The vapour pressure over the solution at 0°C was 1140mm Hg. The volatiles were removed at 20°C and the purple residue pumped on at 3 x 10^{-2}mm Hg for 24 hr. Yield 0.60g. Analysis: Found, Co, 26.15, 26.32; Cl, 15.39, 15.67%. $Coa_5ClF_2.\frac{1}{2}HF$ requires Co, 25.92; Cl, 15.59%.

RESULTS AND DISCUSSION

[Coa$_6$]Cl$_3$ - this luteo salt dissolves readily to form an orange solution (λ_{max} 480nm) in HF, with the loss of HCl which has a low solubility in AHF. The ^{1}H n.m.r. spectrum of the solute at 31.4°C is a broad singlet (width at half-height, $W_{\frac{1}{2}}$, 60Hz), 3.00 ppm downfield from TMS. This singlet becomes sharper at lower temperatures and at -60°C, $W_{\frac{1}{2}}$ = 14Hz and δ= 2.98ppm. The proton resonance line widths of other cobalt ammine complexes in HF show a similar temperature dependence, although minimum line widths were not always found at the same temperature: Jolly et al. [3] have reported similar effects for solutions of $[Coa_6]^{3+}$ in H_2SO_4 and HSO_3Cl and have discussed the mechanisms responsible for the broadening. The variation of proton shifts with temperature in the present study, i.e. over the range -70° to +30°C, was on average 0.05ppm.

$[Coa_5Cl]Cl_2$ - the purpureo chloride dissolves in HF with the loss of only two thirds of the chloride, even at +30°C: the residue compound was shown by analysis to be $Coa_5ClF_2 \cdot \frac{1}{2}HF$. The ^1H n.m.r. spectra of the solute at -60°C in a freshly prepared solution and in a solution previously held at 20°C for several months are identical (δ_4 = 3.32, δ_1 = 2.53ppm).

An absorption at 537nm corresponds to that reported for the chloropentammine complex in water (534 nm) [4]. Evidently this complex cation is much more inert towards AHF than towards 100% H_2SO_4.

$[Coa_5Br]Br_2$ - solutions of this salt in HF absorb at 558nm (552 nm in water [4]) and the -60°C p.m.r. spectrum contains two solute resonances, δ_4 = 3.23 and δ_1 = 2.58ppm. The bromopentamminocobalt(III) ion is also inert to AHF.

$[Coa_5H_2O](NO_3)_3$ - the p.m.r. spectrum of a freshly prepared solution in HF at -60°C showed only two resonances, δ_4 = 3.64 and δ_1 = 2.31ppm. After 7½ min. at 20°C this solution was cooled to -60°C; the new spectrum showed an additional resonance at 1.90ppm, whose intensity was nearly equal to that at 2.31ppm. The total area under the two high field resonances was a quarter of that under the 3.64 ppm resonance; presumably the solvolysis product has δ_4 close to 3.64ppm. No further reaction took place at -60°C; however, when the solution was kept at 20°C for a further 90min. the solvolysis reaction continued to completion. The spectrum of the product consists of δ_4 = 3.68 and δ_1 = 1.90ppm.

The ^{19}F n.m.r. spectrum of the aged solution showed only the solvent resonance (at ca. 190 ppm upfield from $CFCl_3$) at 31.4°C. However, at temperatures below -30°C a new, very broad resonance appeared to high field of the solvent line. The chemical shift at

-60°C was approximately 380ppm upfield from $CFCl_3$ with $W_{\frac{1}{2}}$ = 220Hz. The apparent absence of the F-on-Co(III) resonance at the higher temperatures is probably because of acid-catalysed exchange with the solvent.

A freshly prepared solution of $[Coa_5H_2O](NO_3)_3$ in HF absorbs at 520 and 480(sh) nm: in aqueous solution the aquo complex absorbs at 490nm, whereas the fluoropentammine shows two absorptions in this region, at 514 and 457(sh) nm [4]. Thus it appears that coordinated water is irreversibly solvolysed by AHF according to (1).

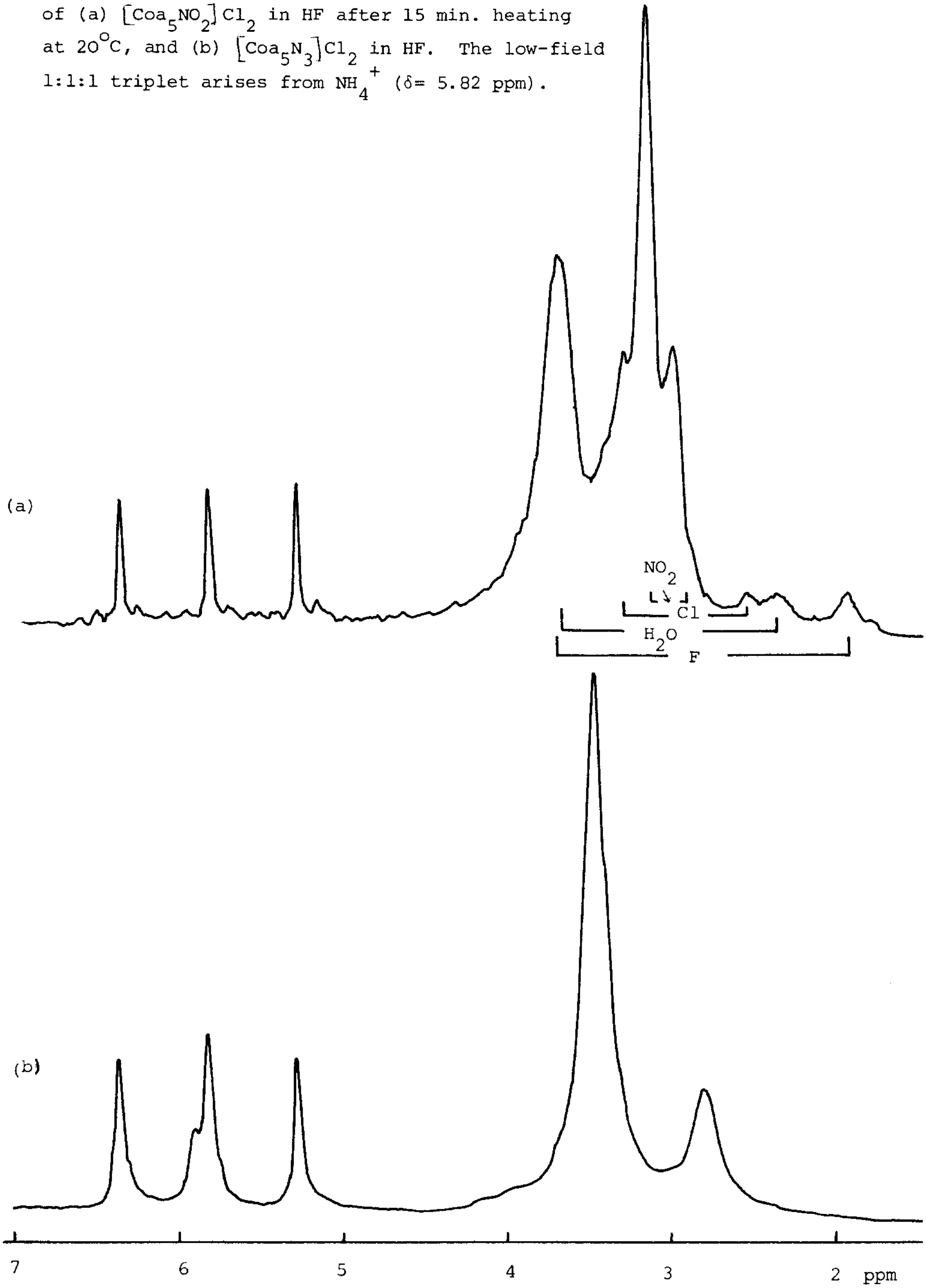
$$[Coa_5H_2O]^{3+} + HF \longrightarrow [Coa_5F]^{2+} + H_3O^+ \qquad (1)$$

$[Coa_5CO_3](NO_3).H_2O$ - this complex dissolves in HF with effervescence, presumably due to loss of CO_2. The properties of the solution were identical with those described for the aquopentammine.

$[Coa_5NO_3](NO_3)_2$ - solutions of this complex behave like those of the aquopentammine.

$[Coa_5NO_2]Cl_2$ - the xantho (nitro) complex in AHF forms an orange coloured solution, which gradully changes through pink to purple at 20°C. The absorption bands in the visible region are initially at 480 and 520(sh) nm; in aged solutions bands at 511 and 530nm gradually appear. It was evident from the ^1H n.m.r. spectra that three reactions were taking place, each with a half-life of about 10 min. at 20°C. All four complexes are evident in the spectrum depicted in Figure 1(a). The fourth product, δ_4 = 3.32 and δ_1 = 2.53 ppm, is evidently $[Coa_5Cl]^{2+}$ and is formed from the third product, $[Coa_5F]^{2+}$, δ_4 = 3.68 and δ_1 = 1.90ppm by the action of HCl (3): this reaction is, at first sight, surprising, however, it confirms that the stability of $[Coa_5Cl]^{2+}$ in AHF is truly thermodynamic and not just kinetic and moreover, is consistent with the lability of F in $[Coa_5F]^{2+}$ in solution in HF. The second complex, δ_4 = 3.64 and δ_1 = 2.31ppm, must be $[Coa_5H_2O]^{3+}$ which reacts according to (1). If the first material, δ_4 = 3.17 and δ_1 = 3.00ppm, is the nitro complex then the sequence of three reactions is (2), (1) and

Figure 1 The -60°C 100MHz ^{1}H n.m.r. spectra of (a) $[\mathrm{Coa_5NO_2}]\mathrm{Cl_2}$ in HF after 15 min. heating at 20°C, and (b) $[\mathrm{Coa_5N_3}]\mathrm{Cl_2}$ in HF. The low-field 1:1:1 triplet arises from $\mathrm{NH_4^+}$ (δ= 5.82 ppm).



(3). The first stage is also known to occur in the solvolysis of $[Coa_5NO_2]^{2+}$ in H_2SO_4[2].

$$[Coa_5NO_2]^{2+} + 2HF \longrightarrow [Coa_5H_2O]^{3+} + NO^+ + 2F^- \qquad (2)$$

$$[Coa_5F]^{2+} + HCl \longrightarrow [Coa_5Cl]^{2+} + HF \qquad (3)$$

$[Coa_5ONO]Cl_2$ - the ^1H n.m.r. spectrum of a freshly prepared solution at -60°C of a sample of the isoxantho (nitrito) complex, which was only 3h old, showed the presence of about 5% of the more stable nitro complex. The main lines in the spectrum were those of the aquopentammine complex which had been generated very rapidly at -60°C. This result is interesting because the nitrito isomer is a possible intermediate in the solvolysis of the nitropentammine in H_2SO_4 [2]. The aquo complex reacts with HF and HCl at 20°C to generate the fluoro and chloro complexes.

$[Coa_5N_3]Cl_2$ - a solution of the azido complex in HF at 20°C absorbs at 508 nm (516nm in aqueous solution [4]). The ^1H n.m.r. spectrum of a freshly prepared solution, Figure 1(b), shows three resonances at 5.90, 3.48 and 2.79 ppm in the intensity ratio 1:12:3. This spectrum is consistent with the protonation of the coordinated azido ligand to form $[Coa_5(N_3H)]^{3+}$, which has been isolated as the perchlorate salt by Monacelli et al. [7]. The detection of the low field resonance, 5.90ppm, assignable to H-on-azide, is consistent with the high basicity of this ligand [8] . Although this protonated complex appears to be moderately stable, it decomposes at 20°C with a half-life of about 1h to form the fluorocomplex, which was itself gradually converted to the chlorocomplex.

$[Coa_5N_3](NO_3)_2$ - a freshly prepared solution of the nitrate at -60°C gave the same solute resonances characteristic of the $[Coa_5(N_3H)]^{3+}$ ion, however, the solution decomposed more rapidly than had been expected at 20°C to form, again, $[Coa_5F]^{2+}$. Reaction (4) may be responsible for the rapid solvolysis, which was complete in 6 min. at 20°C.

$$[Coa_5(N_3H)]^{3+} + NO_2^+ + 2F^- \longrightarrow [Coa_5F]^{2+} + 2N_2O + HF \qquad (4)$$

$[Coa_5CN]Cl_2$ - the cyano complex dissolves in HF to from a stable yellow solution (λ_{max} 448, 400 (sh) nm). The ^1H n.m.r. spectrum at -60°C showed $\delta_4 = 2.86$ and $\delta_1 = 3.72$ ppm, i.e. with the cis-ammine protons resonating to high field of the trans.

CONCLUSIONS

The chemical shifts of the twelve cis-ammine protons (δ_4) and the three trans-ammine protons (δ_1) observed in the course of those studies on pentamminocobalt(III) complexes are listed in Table 1: the singlet resonance of the protons in $[\mathrm{Coa_6}]^{3+}$ is used as the reference. Data for such complexes in 100% sulphuric acid and in d^6-dmso are included. The following trends are evident: (i) δ_4 increases (i.e. moves downfield), (ii) δ_1 decreases, (iii) the difference in chemical shift, ($\delta_4 - \delta_1$), and (iv) the weighted mean chemical shift, ($\frac{4}{5}\delta_4 + \frac{1}{5}\delta_1$) both increase, along the series of ligands X, arranged in the order of increasing electronegativity of the atom bonded to cobalt

$\mathrm{CN^- < NH_3, NO_2^-, NCS^-, N_3^- \sim Br^- < Cl^-\ OH^-, OH_2, O_2CCH_2Cl^-, OSO_3H^- < F^-}$.

Some of these features have been commented upon by other workers[9]: moreover, Nakashima has attempted to correlate the trends for δ_4 and δ_1 with the calculated paramagnetic shielding factors, which in turn relate to ligand field effects [10], cf. [3] and [11].

It is a consequence of the opposing trends for δ_4 and δ_1 that ($\delta_4 - \delta_1$) is particularly sensitive to the nature of X. Nevertheless, the average values of ($\delta_4 - \delta_1$) for X = $\mathrm{CN^-}$, $\mathrm{NO_2^-}$, $\mathrm{Br^-}$, $\mathrm{Cl^-}$ and $\mathrm{OH_2}$ are strikingly solvent-independent. Where X = $\mathrm{CN^-}$ or $\mathrm{NO_2^-}$ it is highly likely that X is either protonated or strongly hydrogen-bonded by the strongly acidic solvents HF or $\mathrm{H_2SO_4}$, however the site for protonation is presumably not the atom bonded to cobalt. A more noticeable change in the value of ($\delta_4 - \delta_1$) does occur when (i) coordinated hydroxide and (ii) coordinated azide are protonated, presumably because the atoms bonded to cobalt are being protonated.

Proton n.m.r. spectroscopy has been found to be a useful analytical technique (i) in establishing the purity of starting materials (e.g. traces of nitro in the nitrato-pentammine complex and of $[\mathrm{Coa_4CO_3}]\mathrm{NO_3}$ in $[\mathrm{Coa_5CO_3}]\mathrm{NO_3.H_2O}$), and (ii) in following the solvolysis reactions described above. UV-visible spectroscopy has not been found to be as powerful a technique in this work as has n.m.r. spectroscopy. Measurements were deliberately confined to the visible region to avoid outside interference from metal-free decomposition products (e.g. $\mathrm{NO^+}$, $\mathrm{NO_2^+}$), although even then impurities absorbing strongly in the visible were encountered.

TABLE 1

^{1}H n.m.r. chemical shift data for $[Co^{III}a_5X]$ complexes in non-aqueous solvents

Solvent	anhydrous hydrogen fluoride				100% sulphuric acid [3]				dimethylsulphoxide [11]				Average value
X	δ_4	δ_1	$\delta_4-\delta_1$	$\frac{4}{5}\delta_4+\frac{1}{5}\delta_1$	δ_4	δ_1	$\delta_4-\delta_1$	$\frac{4}{5}\delta_4+\frac{1}{5}\delta_1$	δ_4	δ_1	$\delta_4-\delta_1$	$\frac{4}{5}\delta_4+\frac{1}{5}\delta_1$	$\delta_4-\delta_1$
$^*NH_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
CN^-	-0.12	0.74	-0.86	0.05	-0.21	0.68	-0.89	-0.03	-0.55	0.33	-0.88	-0.37	-0.88
NO_2^-	0.19	0.02	0.17	0.16	0.00	0.00	0.00	-0.00	-0.03	-0.03	0.00	-0.03	0.06
NCS^-					0.40	-0.05	0.45	0.31					0.45
$^\dagger N_3^-$	0.50	-0.19	0.69	0.36					-0.08	-0.39	0.31	-0.14	0.50
Br^-	0.25	-0.40	0.65	0.12	0.06	-0.42	0.48	-0.04	0.28	-0.37	0.65	0.24	0.59
Cl^-	0.34	-0.45	0.79	0.18	0.17	-0.49	0.66	0.04	0.25	-0.35	0.60	0.23	0.68
OH^-									0.22	-0.53	0.75	0.07	0.75
OH_2	0.66	-0.67	1.33	0.39	0.57	-0.67	1.24	0.32	0.55	-0.57	1.12	0.35	1.23
$O_2CCH_2Cl^-$									0.42	-0.63	1.05	0.21	1.05
OSO_3H^-					0.65	-0.84	1.49	0.35					1.49
F^-	0.70	-1.08	1.78	0.34									1.78

† ^{1}H-on-azide resonance at 2.92ppm in liquid HF

* the singlet resonance of $[Coa_6]^{3+}$ is used as the reference for each solvent.

It may be concluded that when X in $[Coa_5X]^{3+}$ is bonded to cobalt through oxygen, or can isomerise to form a Co-O bond, then the first solvolysis product is $[Coa_5H_2O]^{3+}$. The only complexes which survive the solution process in HF at -60° have X = H_2O, Cl^-, Br^-, CN^-, NO_2^-, N_3^- and F^-. Hydrogen chloride will displace X in $[Coa_5X]^{3+}$ when X = F^- but not when X=CN^-. Complexes which are stable indefinitely in solution in HF include those with X = NH_3, Cl^-, Br^-, F^- and CN^-.

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